

## PATENT SPECIFICATION (11)

1604488

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(54) A METHOD OF MAKING A TRANSPARENCY OR  
 PHOTOGRAPHIC NEGATIVE FROM A  
 RECORD MATERIAL

(71) We, RHONE-POULENC SYSTEMES, a French Body Corporate, of 47, Rue de l'Echat, 94000 Creteil, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of making a transparency or photographic negative from a record material having an opaque pigment layer.

US. Patent No. 3,014,301 relates to a recording material, referred to as a recording chart or chart medium, for use in recording units with a heated or a pressure stylus, and/or a pen containing a solvent. The chart medium is made with a transparent film backing upon which is deposited a white, opaque coating which is heat-, pressure- and solvent-sensitive. The coating is deposited from an unstable solution of nitrocellulose in acetone (a solvent) and xylol (a non-solvent). The whiteness and opacity results from the acetone evaporating first, leaving a high percentage of xylol and nitrocellulose in solution, from which the nitrocellulose is precipitated as a white solid. The chart is made transparent by "printing" the opaque layer with a solvent such as Cellosolve or carbitol acetate from a solvent-dispensing pen. A transparent dye can be added to the solvent to form transparent lines colour-dyed but photographically transparent so that it may be used as a negative for photographic reproduction or as a positive transparency for projection onto screens or other medium. The chart medium can be used, for example, for preparing graphs with conventional pen-operated machines.

A similar sheet record material which is sensitive to pressure is disclosed in U. S. Patent No. 2,962,382, except that water replaces xylol as the high boiling non-solvent and various film-forming polymeric materi-

als such as cellulose acetate, ethyl cellulose and polyethyl methacrylate are disclosed in addition to nitrocellulose as the opaque material. This patent also discloses methyl ethyl ketone and methyl alcohol, in addition to acetone as suitable volatile solvents for the polymeric materials. However, the opaque coatings of this patent require large amounts of surfactant or a combination of surfactant and waxy lubricant to produce useful pressure-sensitive record materials.

While the recording materials described in the above patents provide satisfactory transparencies in many cases they suffer from the drawback that it is very difficult to obtain uniform opaque coatings by depositing a layer of polymeric material from an unstable mixture of volatile solvent and high-boiling non-solvent. Precise control of the rate of evaporation of the volatile solvent is necessary to obtain opaque coatings and uniformity of the opacity over the entire surface. Reproducibility from sheet to sheet is also difficult. Furthermore, the degree of opacity with the polymer/solvent/non-solvent systems of these patents is generally not as high as desirable for good contrast between the transparent film backing sheet and the opaque coating layer.

It has now been found that opaque coatings can be prepared more simply from an aqueous dispersion of finely divided particles of a polystyrene or styrene-based copolymer resin, with a film-forming binder, and that when such an opaque coating is deposited on a transparent backing sheet, positive transparencies for projection of images of the transparent "writing" or negative transparencies for photographic reproduction can be obtained by application of a solvent for the styrene resin particles to the opaque coating.

Accordingly, the present invention provides a method of making a transparency for the projection of information or for making a negative for photographic reproduction of

information, from a record material which comprises a substantially transparent backing sheet covered with an adherent opaque pigment layer, this layer comprising a particulate pigment, having a particle size of between 0.2 to 1 micron, of a styrene polymer which is polystyrene or a styrene-based copolymer, associated with a film-forming polymeric binder, which method comprises inscribing areas of the layer corresponding to the information using a writing point fed by a writing liquid. The invention also includes the use of a record material as defined above in being marked with a writing point fed by a writing liquid comprising a solvent for the styrene polymer pigment.

The parent application No. 20878/78 (Serial no 1604487), out of which the present application has been divided, describes and claims a writing liquid for inscribing information on a record material comprising a support covered with an adherent opaque organic pigment layer. The writing liquid is a defined mixture of a fluorochloroalkane and a solvent for the organic pigment. The invention of the parent application is based on the finding that although fluorochloroalkanes are not generally solvents for organic pigments, it has been found, surprisingly, that a mixture of a fluorochloroalkane with a solvent for the organic pigment is more effective than the solvent used by itself. In particular, all other things being equal, the writing speed is increased for certain mixtures. Fluorochloroalkanes possess a large number of advantages relative to the solvents; they are neither toxic nor flammable, and they have little or no odour.

In the patent application, one form of the invention is a method of inscribing information on the record material and in one embodiment, the record material comprises a transparent backing sheet and a styrene polymer pigment as described above. Accordingly, to avoid overlap of the two cases, the writing liquid used in the present invention is to be regarded as excluding a writing liquid as defined in Application No. 20878/78 Serial no 1604487 (containing a fluorochloroalkane).

As regards the solvents, those skilled in the art will choose them from amongst solvents for the organic pigments used. It is not necessary to choose solvents which are also solvents for the binder used, since suitably skilled persons can formulate layers containing transparent binder resins in a sufficiently small amount not to prevent the solvent from penetrating the layer and solubilising the pigment.

There are certain cases in which it is desired to obtain a coloured trace. In this case, it suffices to mix with the solvent a colorant having the desired shade. By way of indication, there may be mentioned the

colorants sold under the tradename NEO-ZAPAN of Messrs. BASF of those sold under the tradename CERES of Messrs. Bayer, which colorants can be mixed without difficulty with the majority of the suitable solvents.

The opaque pigment layer comprises polystyrenes or a styrene-based copolymer, especially a styrene/butadiene or styrene/acrylic copolymer. The film-forming polymeric binder serves to agglomerate the particles of organic pigment and promote adhesion to the film. Examples of suitable such binders are acrylic resins and polyvinylidene chlorides. The particle size of the organic pigment is important for producing good opaqueness. Particles having a diameter of between 0.2 and 1 micron are used in this invention.

The respective proportions (by weight) of organic pigments and film-forming polymeric binder can vary (within reasonable limits, beyond which limits the opaqueness or other properties of the information support becomes inadequate). The weight ratio of the organic pigment to the total weight of the layer will preferably vary between 0.5 and 0.9, i.e. the proportion of styrene polymer in the opaque pigment layer is preferably 50 to 90% by weight. Plasticisers, optical brighteners, inorganic pigments and the like can also be incorporated in the layer.

This layer may be coated on a transparent support (backing sheet) which can be a film of a natural or synthetic material, e.g. polyethylene, polypropylene, cellulose acetate, polyester or cellulose film, which is substantially transparent or surface-dyed or bulk-dyed. In order conventionally to obtain the desired effect, the weight of solid deposited can vary between 6 and 20 g/m<sup>2</sup> and is preferably from 8 to 14 g/m<sup>2</sup>.

The invention is illustrated by the following Examples. The styrene polymers used comply with the above-stated average particle size requirement.

#### EXAMPLE 1

The following composition:

"Rhodopas" S 051 (polystyrene of Messrs. Rhone-Poulenc)	10 g	115
"IXAN" 91 (polyvinylidene chloride of Messrs. Solvay)	3 g	120

is deposited at a rate of 10 g/m<sup>2</sup> on a polyester film which is sold under the trade mark "Terphane", has a thickness of 75 microns and is covered with an anchoring layer. A product is obtained which has an opaqueness of 60%, as measured with a "Photovolt" type 670 reflectometer. Writing is produced on this film using a tubular point pen which is sold under the trade mark "Staedtler", type Mars 707K and is filled

with methyl ethyl ketone. A perfectly transparent trace is obtained which, on projection, is white on a black background.

5 If a blue colorant such as crystal violet is added to the solvent, a blue trace is obtained directly on a black background, and if the crystal violet is replaced by "Organol Yellow PC", sold by Messrs. Uguine Kuhlmann, a yellow trace is obtained.

10 An equally good result is obtained by substituting the methyl ethyl ketone by toluene, ethyl acetate or methylene chloride.

#### EXAMPLE 2

15 "Pliolite" latex 151  
(styrene/butadiene copolymer  
of Goodyear) 10 g  
20 "Diofan" 3033  
(polyvinylidene chloride  
of BASF) 3 g

are deposited on a 50 micron thick polyester film of the kind described in Example 1. A product is obtained which is essentially equivalent to that described in Example 1.

In order to write on the record material, the procedure of Example 1 can be followed exactly or the body of a felt pen of the "Onyx" marker type of Messrs. Baignol and Farjon can be filled with any one of the solvents mentioned in Example 1 to give equivalent results except that the writing is wider.

35 The words "Rhodopas", "Ivan", "Terphane", "Staedtler", "Pliolite" and "Cello-solve" are registered trade marks.

#### WHAT WE CLAIM IS:—

40 1. A method of making a transparency for the projection of information or for making a negative for photographic reproduction of information, from a record material which comprises a substantially transparent backing sheet covered with an adherent opaque pigment layer, this layer comprising a particulate pigment, having a particle size of between 0.2 to 1 micron, of a styrene polymer which is polystyrene or a styrene-based copolymer, associated with a film-forming polymeric binder, which method comprises inscribing areas of the layer corresponding to the information using a writing point fed by a writing liquid comprising a solvent for the styrene polymer pigment other than a writing liquid defined in any claim of Application No. 20878/78 Serial no 1604487.

2. A method according to claim 1 wherein the weight proportion of styrene polymer in the opaque pigment layer is from 50 to 90%.

3. A method according to claim 1 or 2 wherein the film-forming polymeric binder is an acrylic resin.

4. A method according to claim 1 or 2 wherein the film-forming polymeric binder is a polyvinylidene chloride.

5. A method according to claim 1, 2, 3 or 4 wherein the solvent is methyl ethyl ketone, toluene, ethyl acetate or methylene chloride.

6. A method according to claim 1, substantially as described in Example 1 or 2.

7. A record material defined in any preceding claim marked with a writing point fed by a writing liquid comprising a solvent for the styrene polymer pigment, other than a writing liquid as defined in any claim of Application No. 20878/78.

8. A transparency or photographic negative when made by a process claimed in any one of claims 1 to 6.

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